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## Failure Rate Model For Cathodic Delamination of Protective Coatings

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## FAILURE RATE MODEL FOR CATHODIC DELAMINATION OF PROTECTIVE COATINGS

### INTRODUCTION

The specific problem addressed in this report is the cathodic delamination of rubber-to-metal bonds used in wet-end sonar components to provide watertight integrity of those components. Failure rate modeling is the terminology we use to describe the development of quantitative relationships between times-to-failure ( $t_f$ ) and the magnitude of the environmental forces acting on components of interest. A major objective of this report is to demonstrate how failure rate modeling can be applied to current fleet problems for the purpose of predicting the reliability and service life of a design feature. When, as in the case of the rubber-to-metal bond used in the Portsmouth connector, a design feature is found to be flawed, the failure rate model facilitates the evaluation of the impact on reliability and life of alternate design solutions.

Cathodic protection of painted metals is very common to reduce metal corrosion in marine service. Virtually every steel ship in the U.S. fleet is protected in this way, by the deployment of zinc anodes electrically attached to the hull in many locations. The zinc anodes corrode sacrificially thereby protecting the steel which becomes the cathode wherever it is in contact with the seawater electrolyte. The benefits of cathodic protection are enormous - steel hulls would be quite short-lived without it.

There are problems, however, associated with the cathodic reactions which can lead to the progressive, spontaneous delamination of rubber-to-metal bonds, particularly if the metal is more noble than the steel hull. A case in point is the Portsmouth connector which has a Monel (approximately 70% nickel and 30% copper) backshell to which is molded a polyurethane boot. Connector flooding by the ingress of water up the outside and down the inside of delaminated molded boots has been observed recently in as little as a year of submarine service.

We will provide background on current explanations of the cathodic delamination process, and offer a description of our weak boundary layer model. With the major objective of this report in mind; e.g., demonstration of a method, the final equations of our cathodic delamination model are the results of simplifying assumptions made so that closed-form expressions can be written down. Before truly correct quantitative relationships can be developed, an experimental program such as that outlined in this report must be executed.

The most important conclusion to the work described in this report is that it is feasible to understand and quantify failure processes in substantial

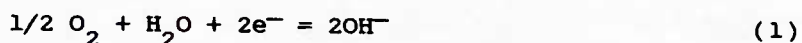


detail. Since cathodic delamination is an important problem in Navy sonar applications, we recommend that a modest experimental investigation of the process be conducted and the needed quantitative relationships be established. In addition, we recommend that attention be given to the improvement of testing procedures. With improved understanding and better test procedures, the evaluation of reliability and life of future candidate rubber bonding systems will be more accurate.

## BACKGROUND

Although it has been the object of considerable study, the exact nature of the polymer-to-metal bond is not indisputably agreed upon. Dispersion forces that occur when two surfaces are brought within 1 nm of each other are very important. In fact, calculations of ideal dispersion forces are often quoted as proof that if two phases are in intimate molecular contact, dispersion forces alone are sufficient to account for the observed strengths of adhesive bonds [1-5]. This explanation requires ideal contact, without exception or fault. Small defects and contaminants on the mating faces of an adhesive and the substrate are inevitable and will result in reduced adhesion. Therefore, it is likely that dispersion is insufficient to account for all of the observed strength of adhesion. Other explanations of the nature of the polymer-to-metal bond include: mechanical adhesion due to microscopic physical interlocking of the two faces, chemical bonding due to acid base reactions occurring at the interface, hydrogen bonding at the interface, and electrostatic forces built up between the metal face and the dielectric polymer. It is reasonable to assume that all of these kinds of interactions, to one degree or another, are needed to explain the failure of adhesion in the cathodic delamination process.

During the cathodic delamination process there are two important reactions which can occur at the cathode and which are catalyzed on the thin layer of metal oxide which covers the cathode surface. These reactions are



and



Either reaction will result in an increase of the pH near the reaction site. Which reaction predominates depends upon the circumstances. The equilibrium potential for the oxygen reduction reaction is 1.24 V more positive than the equilibrium potential for hydrogen reduction. However, the exchange current densities for hydrogen evolution on corrodible metal surfaces are far greater than the corresponding values for oxygen reduction. The cathode polarization curve for steel in 0.5 M saltwater [6] demonstrates that the oxygen reduction reaction is favored at potentials less than -0.8 V (vs a standard calomel electrode) and the hydrogen reduction reaction is favored at potentials more negative than -1.0v. Thus, in neutral or basic solutions, where the  $\text{H}_3\text{O}^+$  concentration is low, where dissolved oxygen is present, and where an applied voltage less than -0.8 V is present, we expect to find the oxygen reduction reaction dominating.

Cathodic delamination is an active area of research. It is generally agreed [7-9] that the formation of the  $\text{OH}^-$  is a crucial element for delamination. As long as there is a growing pocket of caustic solution sequestered between the coating and substrate layers, further delamination is occurring. However, this is where the agreement ends. The actual mechanism by which  $\text{OH}^-$  instigates the debond is not clear. Various theories exist. A review [9] of current advances identifies three principal mechanisms:

1.  $\text{OH}^-$  attack of polymer which weakens or displaces polymer/metal oxide bonds.
2.  $\text{OH}^-$  attack of the metal oxide. The metal oxide will dissolve in  $\text{OH}^-$  solutions when the concentration becomes high enough.
3. Loss of adhesion by the intervention of water at the interface.

In support of the first mechanism, using surface analysis techniques, Dickie, Hammond, and Holubka [10] have reported that carboxylated species present at the interface can be seen as a result of  $\text{OH}^-$  attack of the polymer. On the other hand, Leidheiser [9] reports that Ritter has observed attack of the metal oxide using ellipsometric techniques to study a polybutadiene coating on steel. Ritter and Kruger [11] have measured pH values as high as 14 at the delamination site under natural corrosion conditions. This is certainly high enough to cause the dissolution of some metal oxides. Koehler [12,13] has recently presented arguments for the case that the root cause of cathodic delamination is the displacement of the coating by a high pH aqueous film that grows in the interfacial region.

Explanations of failure are heavily influenced by the individual researcher's belief in what kind of interaction is principally responsible for the adhesion. If it is thought that dispersion forces represent the principal strength of the bond then Koehler's approach will be favored. In that description the interfacial water would drastically reduce the dispersion forces between polymer and metal. If hydrogen bonding and acid base reaction bonds are the most important force then the  $\text{OH}^-$  attack of the polymer or metal oxide would be of major importance. As a secondary effect, the corrosion products of these attacks would also contribute to the reduction of the dispersion forces between polymer and metal.

A possible starting point in developing a quantitative model for failure would be to assume that all three of the described mechanisms are contributing to the overall debonding to one degree or another. However, a recent review [14] of the current state of failure mechanism descriptions by Leidheiser points to a deficiency shared by all three. None of the mechanisms account for the absence of irreversible delamination in strong sodium hydroxide solutions. All three explanations predict that with increasing concentrations of NaOH the delamination should be accelerated. Yet, when a polymer-coated metal substrate is first completely immersed in a NaOH solution with a pH greater than 10 and then the sample is allowed to dry before applying a peel test, such as the Scotch® tape test, no delamination is observed.

In the next section we will introduce an additional feature to the mechanism which may explain the apparent anomaly. By incorporating this

feature with the other explanations we arrive at a composite mechanism for delamination. From this can be derived a mathematical model of the delamination which we will call the weak boundary layer model since it draws upon Bikerman's weak boundary layer theory [15]. This model does not deny the utility of the other models, it builds upon them; and, in addition, it offers a rationale for the behavior of the coatings in high pH electrolytes.

In the next section the chemical equations and their respective rate equations will be employed to obtain a quantitative description of the rate of delamination. We will show how it is possible to determine the rate of delamination in terms of measurable characteristics of the component materials. We will follow that with a section on the experimental requirements and some testing approaches which could be used to define material reliability and aging characteristics with respect to failure by cathodic delamination.

#### **WEAK BOUNDARY LAYER MODEL**

From the point of view of accelerated life testing and reliability testing of wet-end sonar equipment, the current literature on cathodic delamination, though rich in content, falls short of our needs. The available interpretations help us to understand the failure mechanism in only a qualitative way. What is needed is an exact quantitative understanding of the rate of delamination as a function of environmental forces. Such an understanding would lead to strategies for component selection and optimization of maintenance procedures, as well as accurate predictions of service life and reliability. The objective of this section is to present a more plausible explanation of cathodic delamination and show that it is possible to obtain a model from it which describes the rate of delamination in terms of measurable characteristics of the polymer, the metal, and the environment.

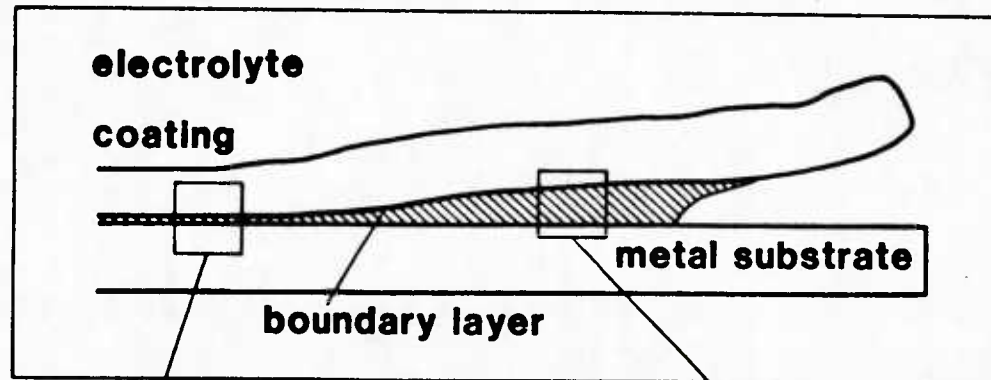
A visualization of the cross section of a delamination process is shown in Fig. 1(a). The figure shows a cathodically polarized metal substrate under a polymeric coating where some delamination has occurred. The metal surface may be exposed and in contact with the electrolyte by design as in the connector boot/backshell/seawater interface of the Portsmouth or the TR-317 connectors, or by accident as in a pin hole in the TR-317 face rubber, or a chip on a painted housing. It is also possible for a cathodic reaction to proceed without overt exposure to the electrolyte, as in the case of blistering. In the zone of delamination the catalytic reduction of oxygen proceeds as in Eq. (1). The reaction produces  $\text{OH}^-$ . Indisputably, the concomitant buildup of a high pH environment is of major importance. In an experiment to analyze the cathode environment, Ritter and Kruger [11] inserted pH electrodes through the back of the metal surface into the interfacial region and found the pH was as high as 14. Above pH 11 the dissolution of some metal oxides can take place and, undoubtedly, the breaking of hydrogen bonds and acid-base bonds can take place. However, these possible effects resulting from a high pH are not sufficient to explain why delamination does not take place when the bulk electrolyte has a high pH. In order to develop a hypothesis to explain the anomalous behavior we will look closely at the details of the delamination process.



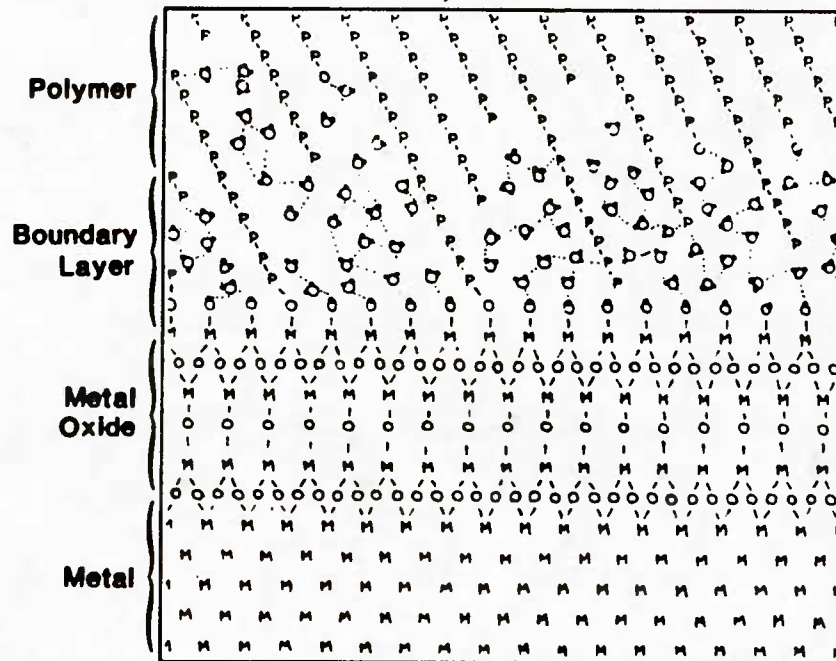
In Fig. 1(b) we present a more elaborate cross-sectional view of a possible delamination geometry. This blowup of a segment of the interface is adopted from a diagram of Minford [16]. The substrate is a metal with a high-energy surface such that it is nearly impossible to prepare the surface for coating without an oxide layer appearing. The oxide layer forms very quickly from oxygen in the atmosphere and is then partially reduced to hydroxide in the presence of moisture in the atmosphere. Although the presence of an oxide layer may reduce adhesive strength, it may be desirable to some extent from the point of view of corrosion resistance to the flow of electrons. Not only will exposure to the atmosphere result in a layer of metal oxide but also water vapor in the air is adsorbed rapidly—so much so that apparently dry metal surfaces have been reported [17] to hold as many as 27 layers of water molecules! The water molecules are interlocked in a three-dimensional array by hydrogen bonding. There is a transitional boundary between the metal oxide layer and the polymeric coating, which connects the polymer ends, the water, and possible contaminants to the metal oxide. The polymer molecules in the interphase (fancifully drawn here as strings of P's) are linked to the metal oxides by direct hydrogen bonding, indirect hydrogen bonding through the water, and direct polymer-to-metal bonds of some variety.

Recent work at the Texas Research Institute, Inc. (TRI) [18] and at General Dynamics' Electric Boat Division (GD/EB) [19] has suggested that the amount of moisture in the polymer has a profound effect on the bonding system. The GD/EB studies showed that free films of Chemloc 205 and 220 (as well as others) adsorbed more water (by a factor of 3 to 1) when immersed in 0.1 molar NaOH than when immersed in fresh water or artificial seawater. The TRI work showed that the Chemloc 205/220 bonding system lost wet adhesive strength to mild steel substrates, in the absence of coating defects, in pH 13 NaOH at 20°C with an absence of corrosion activity. Thus the presence of OH<sup>-</sup>, in super abundance at the surface of the polymer, enhances the ability of the polymer to absorb water. When the interface between the polymer and the metal becomes concentrated in OH<sup>-</sup>, water will diffuse into the boundary region. This water will reduce the dispersion force between the surfaces as well as feed the swelling of the polymer at the attachment surface. Figure 1(c) attempts to illustrate how the abundance of water strains the polymer-to-metal bonds. Eventually the localized swelling will reach a critical level and the remaining polymer-to-metal oxide bonds in the delamination zone will not be able to support the mechanical peel (mode I) or shear (mode II) stresses created by the distortion of the polymer. At this point the polymer will detach itself still further from the metal, exposing an increased area of catalytic metal oxide surface for further oxygen reduction. The further the polymer debonds, the deeper will be the abscess where OH<sup>-</sup> can accumulate. Of course, the more water that is drawn in, the more exaggerated becomes the local swelling and the further the polymer delaminates. The process will continue, more or less continuously, paced by the kinetics of the diffusion of water, Na<sup>+</sup> and O<sub>2</sub> to the reaction site.

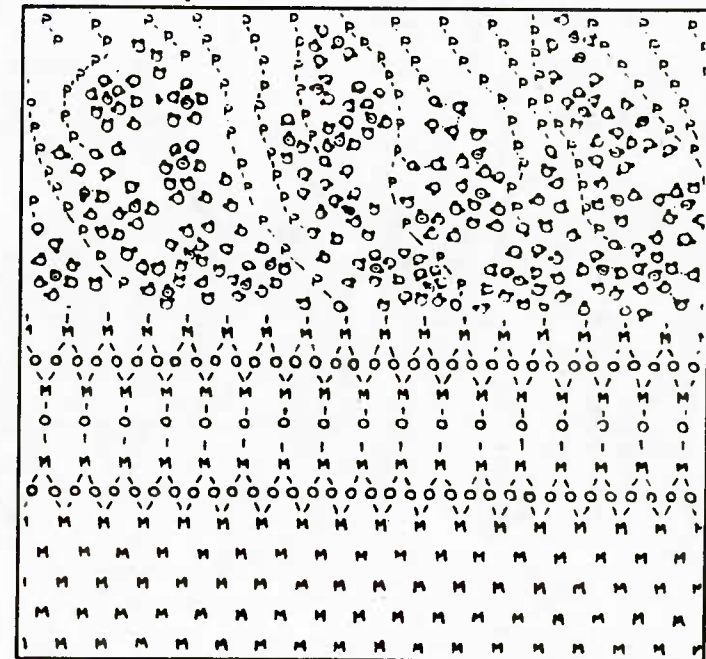




(a) The delamination



(b) The boundary layer



(c) The delaminating zone

Fig. 1 - The changes in the boundary layer during delamination

All this evidence points to the conclusion that  $\text{OH}^-$  acts to force the polymer to become supersaturated with water. The delamination is a result of the increased presence of water in the boundary layer. The water weakens the polymer-to-metal bonds through swelling. In addition, the water reduces the dispersion forces between the layers as first proposed by Castle and Watts [20] and advocated by Koehler.

This explanation predicts that, in some cases, reversible delamination could be observed. The delamination is caused by mechanical stress set up by the swelling of the polymer. In some situations the dispersion forces between the layers may not be permanently disrupted by the formation of residues left by the  $\text{OH}^-$  attack of the metal oxide, the  $\text{OH}^-$  attack of the polymer, or the precipitation of pH-sensitive solutes from the electrolyte. In this case, if the swollen, delaminated polymer is carefully allowed to dry, some of the original polymer-to-metal interaction would re-establish itself. The extent of the repair would depend on the importance of dispersion forces and the ability of the polymer to flow locally to re-establish contact. Evidence in support of this prediction was supplied by the aforementioned work at TRI and GD/EB where it was observed that the wet tensile strength of these free-film adhesive specimens was shown to be reduced as a direct function of moisture absorption and this effect was largely reversible. When carefully dried, the specimens regained their original tensile strength.

Also, corroborating evidence has been reported recently by Koehler [12]. He observed that when the metal/polymer sample was immersed in a sodium hydroxide solution of pH 11.7, wet adhesion was lost. The wet polymer delaminated microscopically even though attack of the metal oxide had not taken place. After drying, it was found that adhesion was regained.

In summary, we surmise that the production of  $\text{OH}^-$  by the cathodic reaction increases the ability of the polymer to absorb water. This must be due to surface energy effects because the chemical potential of water in the aqueous sodium hydroxide should be less than in fresh water based on solution theory. Arguments that the hydroxide is hydrolyzing the polymer are clearly invalid because of the fact that the free polymer films regain their original dry strength after exposure and drying out. The absorption of extra water surely places at least a portion of that water at the interface which creates a weakened boundary. Eventually the boundary layer becomes sufficiently water-saturated and the bond will fail at the interface when any additional mechanical stress is applied; for instance, stress due to a peel test or distortion of the coating due to swelling.

The swelling due to a localized concentration gradient helps to explain the anomalous behavior in NaOH electrolytes. When a thin polymeric coating is immersed in a strong NaOH solution the polymer is uniformly wetted by the  $\text{OH}^-$ , thus it becomes uniformly swollen. No concentration gradient exists between the pocket of  $\text{OH}^-$  in the boundary layer and the bulk of the electrolyte across the coating. Therefore, there will be reduced mechanical stress in the polymer; there will be less peeling or shearing action. Without the delamination due to non-uniform swelling there will be no new surfaces exposed for  $\text{OH}^-$  attack of the metal oxide or polymer. No corrosion products will form. Without corrosion products, any weakening of the polymer/metal interaction, due to the surface energy changes, is reversed when the polymer is dried.

It is hoped that this proposed explanation has incorporated the best features of the previous descriptions and conciliated them with the anomalous behavior of polymer adhesion in a high pH electrolyte. It is essential to identify the correct mechanism to develop an accurate model for service life time predictions and also to have a sound basis for decisions to improve coatings and adhesive formulations. This explanation is in line with the known experimental evidence and is not at odds with the standard descriptions of cathodic delamination, each of which certainly reflects some aspect of the true circumstances. Therefore, we believe it would be worthwhile to employ this explanation in the derivation of a quantitative, mathematical model from the proposed rate processes that lead to delamination.

The rate processes that lead to cathodic debonding are the following. On the catalytic surface of the metal oxide the reduction of oxygen takes place. The rate of this reaction depends on the availability of electrons or the potential of the metal substrate, and the availability of water and oxygen at the interface. The rate at which  $\text{OH}^-$  can be produced also depends on the rate at which the concentration gradient draws water along the boundary and the availability of cations to neutralize the charge. There exists a self-enhancing feature here whereby the faster water is drawn along the boundary carrying  $\text{O}_2$  and  $\text{Na}^+$  to the reaction site, the greater the local swelling; this leads to more delamination which, in turn, exposes more surface area for increased production of  $\text{OH}^-$ . The rate processes leading to debonding are summarized in Fig. 2.

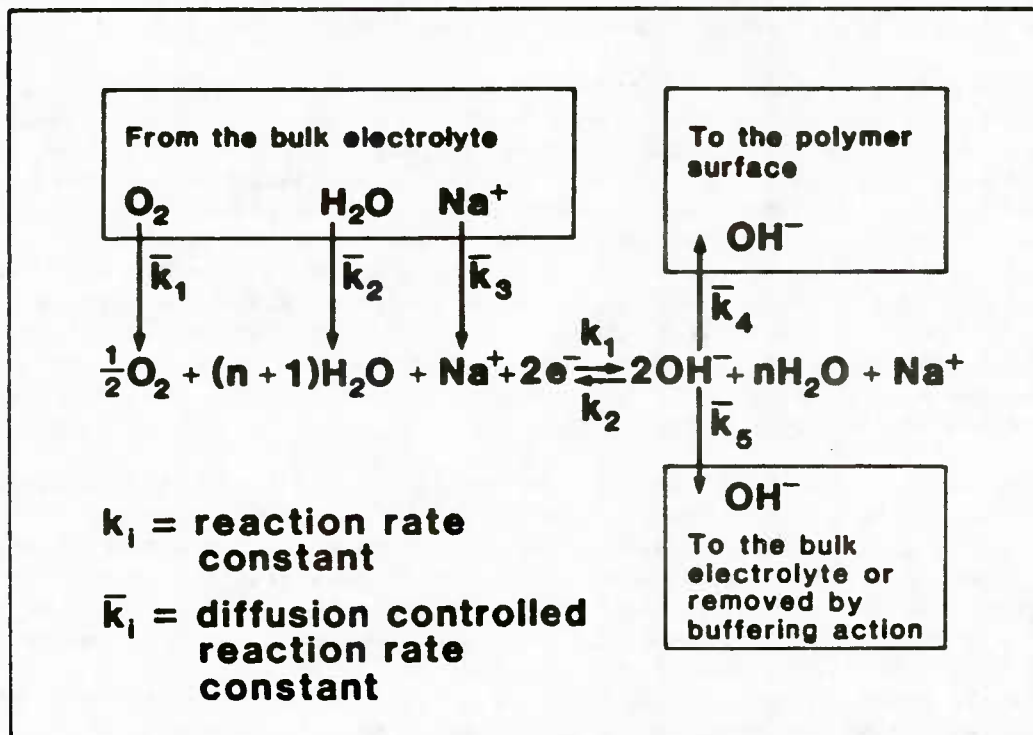


Fig. 2 - The rate processes leading to debonding.

At the reaction site the following processes take place;

$$\begin{aligned} \frac{\partial[\text{OH}^-]}{\partial t} = & k_1[\text{O}_2]^{1/4}[\text{H}_2\text{O}]^{1/2}[\text{e}^-] - k_2[\text{OH}^-] \\ & - (\bar{k}_3 + \bar{k}_5)\nabla^2[\text{OH}^-] + \bar{k}_4\nabla^2[\text{Na}^+] , \end{aligned} \quad (3)$$

$$\begin{aligned} \frac{\partial[\text{H}_2\text{O}]}{\partial t} = & -k_1[\text{O}_2]^{1/4}[\text{H}_2\text{O}]^{1/2}[\text{e}^-] + k_2[\text{OH}^-] \\ & + \bar{k}_2\nabla^2[\text{H}_2\text{O}] , \end{aligned} \quad (4)$$

$$\frac{\partial[\text{H}_2\text{O}]}{\partial t} = -k_1[\text{O}_2]^{1/4}[\text{H}_2\text{O}]^{1/2}[\text{e}^-] + \bar{k}_1\nabla^2[\text{O}_2] . \quad (5)$$

At the delamination site the following processes take place

$$\frac{\partial[\text{H}_2\text{O}]}{\partial t} = \bar{k}_2\nabla^2[\text{H}_2\text{O}] , \quad (6)$$

$$\frac{\partial[\text{OH}^-]}{\partial t} = \bar{k}_5\nabla^2[\text{OH}^-] . \quad (7)$$

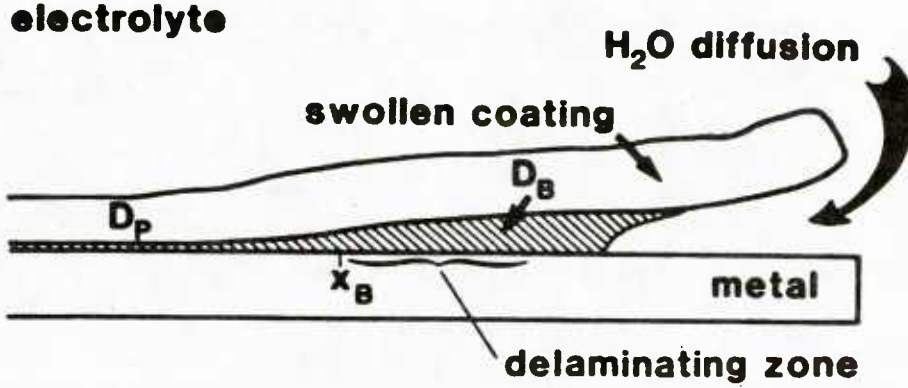
Equations (6) and (7) are coupled to Eqs. (3) through (5) by the boundary conditions at the interface. In order to derive an expression for the rate of delamination from such a complex set of interactions we must make some simplifying assumptions. These could be discarded later once the numerical machinery was in place to handle the complications.

It is our goal here to show that, in principle, a relationship can be derived to give quantitative information about the rate of delamination. For the purpose of illustration, we will approximate the simultaneous solution to Eqs. (3) through (7) by assuming that the diffusion of water to the reaction site, Eq. (6), is the rate determining step. We already know that the water is of primary importance; it carries  $\text{O}_2$  and  $\text{Na}^+$  to the reaction site, it lowers the osmotic pressure, and it swells the polymer, straining all the chemical bonds and disrupting dispersion forces. All this does not prove water diffusion is the rate determining step, but it is a reasonable assumption with which to make an illustration.

Thus, we will restrict our attention to the diffusion of water through two regions depicted in Fig. 3:

1. The boundary layer with diffusion constant  $D_B$ .
2. The polymer coating along the interface beyond the delamination zone with diffusion constant  $D_P$





Shaded area denotes the BOUNDARY LAYER.

Fig. 3 - The growing boundary layer with diffusion constant  $D_B$  and the polymer coating with diffusion constant  $D_p$ .

The diffusion of water in polymers satisfies Fick's laws [21]. Thus, the concentration of water in a polymer will satisfy

$$\frac{\partial c}{\partial t} = D_p \frac{\partial^2 c}{\partial x^2} . \quad (8)$$

Before the cathodic reaction is initiated at a defect, the polymer will be saturated with water from the electrolyte.

$$c = C_p^S \quad (\text{initial condition}) . \quad (9)$$

A general solution to Eq. (8) which satisfies the initial condition is given by

$$c = C_p^S + A \operatorname{erfc} \left( \frac{x}{2D_p^{1/2} t^{1/2}} \right) . \quad (10)$$

After cathodic reaction starts, a weakened boundary layer along the polymer and metal interface begins to form and propagate. The concentration of water in this layer is assumed to satisfy a similar differential equation,

$$\frac{\partial c}{\partial t} = D_B \frac{\partial^2 c}{\partial x^2} . \quad (11)$$

At the opening to the electrolyte, the boundary layer will be supersaturated with water,

$$c = C_B^{SS} \quad \text{at } x = 0 . \quad (12)$$

A general solution to Eq. (11), satisfying Eq. (12), is given by

$$c = C_B^{SS} - B \operatorname{erf}\left(\frac{x}{2D_B^{1/2}t^{1/2}}\right). \quad (13)$$

Let the boundary between the firm polymer and the gelatinous boundary layer be designated  $X_B$ . We will define  $X_B$  to be the point at which the concentration of water in the polymer is sufficient to cause loss of wet adhesion. Let this concentration be denoted  $C(X_B)$ . Then in the polymer at  $X_B$ ,

$$C(X_B) = C_P^S + A \operatorname{erfc}\left(\frac{X_B}{2D_P^{1/2}t^{1/2}}\right), \quad (14)$$

and in the boundary layer at  $X_B$ ,

$$C(X_B) = C_B^{SS} - B \operatorname{erf}\left(\frac{X_B}{2D_B^{1/2}t^{1/2}}\right). \quad (15)$$

Equations (14) and (15) fix the constants A and B. A summary of the relation between concentration of water and distance from the opening is presented in Fig. 4.

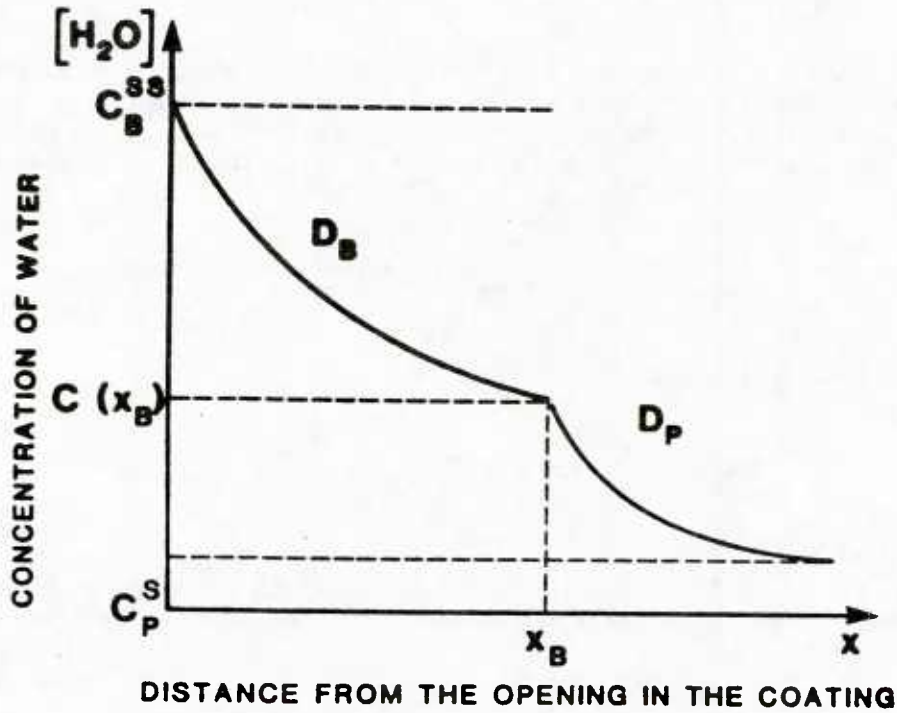


Fig. 4 - The concentration of water as a function of distance from the opening in the coating. The diffusion constant in the polymer at distances greater than  $x_B$  is  $D_P$ . The diffusion constant in the boundary layer is  $D_B$ .

At any given time the flux of water into the face of the boundary surface at  $x_B$  must equal the flux of the water moving out of the surface at  $x_B$ . Thus,

$$D_B \left[ \frac{C}{x} \right]_{\text{layer at } x_B} = D_P \left[ \frac{C}{x} \right]_{\text{at } x_B} \quad (16)$$

Thus,

$$D_P^{1/2} A \exp \left[ \frac{-x_B^2}{4D_P t} \right] = D_B^{1/2} B \exp \left[ \frac{-x_B^2}{4D_B t} \right] \quad (17)$$

For this conservation of matter equation to hold for all values of time, the boundary point  $x_B$  must be moving according to

$$x_B = 2\gamma D_P^{1/2} t^{1/2} \quad (18)$$

Where  $\gamma$  is some proportionality constant.

Substituting Eq. (18) into Eq. (17) and using the definitions of A and B in Eqs. (14) and (15) we find  $\gamma$  is a solution to

$$\phi^{1/2} \left[ \frac{C(X_B) - C_P^S}{\operatorname{erfc}(\gamma)} \right] \exp(-\gamma^2) = \left[ \frac{C_B^{SS} - C(X_B)}{\operatorname{erf}(\gamma\phi)} \right] \exp(-\gamma^2\phi), \quad (19)$$

where

$$\phi = \frac{D_P}{D_B}.$$

That this model is at least qualitatively correct is confirmed by the results of Leidheiser, Wang and Igetoft [6] who empirically found that the radius of delamination was proportional to the square root of time. It remains to be seen if the proportionality constant is equivalent to  $2\gamma\sqrt{D_P}$ . In the next section we will discuss exactly what kinds of experimental procedures will be necessary to establish the validity of the rate of delamination.

Equation (18) represents the rate of delamination for our somewhat simplified initial analysis of the mechanisms. However, it would be possible to solve all of the differential equations for the rate processes simultaneously in order to calculate the concentration of water as a function of time,  $O_2$  availability, metal oxide catalytic surface type, susceptibility of polymer bonds to  $OH^-$  attack, permeability of coating, etc. In addition, the diffusion of water would be more realistic if it was solved in two dimensions, imitating the radial diffusion of water which has entered the interface through a defect in the coating. These improvements would result in a powerful model that will even more accurately reflect realistic service and environmental parameters.

#### RECOMMENDED EXPERIMENTAL APPROACH

The experimental procedures envisioned would first evaluate the failure model and then explore the refinement of it as a realistic picture comes into focus. The delamination process was illustrated in Fig. 2. From that figure it can be seen that we need to measure the following rate constants:

- $k_1$  The rate constant for the reduction of oxygen catalyzed by the substrate, evaluated for a range of cathodic potentials.
- $k_2$  The rate constant for the back reaction caused by a buildup of reaction products in the boundary layer.
- $\bar{k}_1$  The rate constant for the diffusion of oxygen through (1) the coating and (2) the boundary layer.



- $\bar{k}_2$  The rate constant for the diffusion of water through the (1) coating,  $D_p$ , and through the (2) boundary layer,  $D_B$ .
- $\bar{k}_3$  The rate constant for the diffusion of the charge neutralization cation through (1) the coating and (2) the boundary layer.
- $\bar{k}_4$  The rate constant for the diffusion of  $OH^-$  from the reaction site, through the boundary layer to the polymer interfacial surface. Sophisticated treatment of this step would break it down into a multistep, multidirection, reaction to include the effect of  $OH^-$  on the surface energy of the polymer, and the attack of polymer to metal bonds.
- $\bar{k}_5$  The rate constant for the diffusion of  $OH^-$  from the reaction site to the bulk electrolyte through (1) the coating and through (2) the boundary layer. It will also be useful to evaluate the effect of reducing the  $OH^-$  concentration by the use of buffering agents in the polymer.

It will also be necessary to measure:

- $C_P^S$  The concentration of water in the polymer a long way from the reaction site.
- $C(X_B)$  The concentration of water at front of the delamination zone.
- $C_B^{SS}$  The concentration of water in the boundary layer directly exposed to the electrolyte.

Finally, it will be necessary to devise some kind of technique capable of detecting the moving front of the delamination zone,  $X_B$ . It would be most useful if a nondestructive method could be found such that continuous monitoring of the process would be available.

Standard electrochemical measurements can be employed to relate the current density to the applied potential. Performing these measurements under controlled conditions will enable us to determine the rate constant for the reduction of oxygen reaction (i.e.  $k_1$ ). Initial rates, before product buildup occurs, will fix the forward reaction,  $k_1$ ; and then, from curves for the current with respect to hydroxide ion concentration, we can calculate the backward reaction rate constant,  $k_2$ .

An assortment of diffusion rate constants are needed. Some will be routine measurements; some may prove to be difficult to pin down, such as diffusion rates through the boundary layer; and others may be available in the literature.

Routine measurements include the diffusion constants for the diffusion of oxygen,  $\text{Na}^+$ ,  $\text{OH}^-$  and water through the polymer coating. The usual procedure is to establish a steady state permeation across the polymer membrane to be characterized. The rate of transfer of water can be obtained by periodic weighing. Diffusivity is obtained from the initial slope of the weight gain plotted against the square root of time. For the case of oxygen diffusion, Leidheiser has perfected a simple test procedure [6] which artificially makes oxygen diffusion through the coating, or through the boundary layer, the rate-controlling factor. He measures the current flow as a function of oxygen availability. Similar testing approaches would work for  $\text{Na}^+$  and  $\text{OH}^-$ . All the rate constants can be evaluated at a series of temperatures so that activation energy for each diffusion reaction step can be obtained. Assuming the Arrhenius dependence on temperature, the effect of aging on the competing steps of the mechanism could be calculated.

Monitoring the movement of  $X_B$  could most easily be done with an interferometric technique such as the one used by Liechti [22] to view the progress of crack development in polymers. Such measurements might be obtained by coating the polymer surface with a birefringent. When viewed under suitably polarized light, sensitive measurements of the swollen area could be made and recorded as a function of time.

Contributions to the rate of the overall reaction by the diffusion of the reactive species through polymer coating of different thicknesses is relatively easy to account for. However, if diffusion along the boundary layer is a decisive factor, the effect of the shape, size, and quality of the opening into the interfacial region may be more difficult to account for. In fact, this could necessitate a separate analysis of the kinetics of every kind of surface defect encountered. The influence of geometric configuration on corrosion reactions in a marine environment has been ambitiously tackled before. Kasper and April [23] have applied a general finite element modeling procedure to the problem of calculating the electrogalvanic field due to multiple anodic/cathodic reactions taking place in a variety of realistic three-dimensional geometries. This work provides encouragement that, should the need arise, it would be possible, to some extent, for important design features to take into account the shape of the polymer-to-metal interface.

Once the data is gathered and the model is tested and refined, it will be possible to see how the kinetics of the delamination are controlled by a large number of material and environmental variables. Control of the variables will lead to control over the delamination front,  $X_B$ . For instance, the  $\text{OH}^-$  concentration may be controlled with buffers added to the polymer; the electro-osmotic gradient may be reduced by allowing the metal oxide layer to be thicker, increasing the resistance to charge migration; the preparation of the metal substrate, by degreasing or abrasive cleaning, alters the nature of the boundary layer; the catalytic surface can be changed by treatment with  $\text{Co}^{++}$  which acts as an electron sink; the thickness of the coating can be used to control rates of diffusion through the surface; and the swelling of the coating can be reduced by selecting polymers with less permeability to water. The list of variables has in no way been exhausted.

The general area of quantitative understanding of polymer-to-metal adhesive strength through the use of standardized tests has been neglected for the most part. A major problem, in particular, is the degree of adhesion for the thicker kinds of coatings. According to Leidheiser [9] the cross-cut test

is used with some kind of success only on coating less than 100 microns thick. The impact test of Zorll [24] is also useful only for coatings less than 100 microns. Vertical tear-off tests do not work for thick inflexible coatings. Nothing is available for the thicker coatings. One possibility is Funke's suggestion that water absorption by free films compared with water absorption of the same material on metal backing can be used to diagnose loss of adherence. Funke [25] has shown that some coating materials gain more weight when coated on a metal plate and immersed in water than when immersed in water as free films. He has gathered evidence that cross overs in absorption vs time curves indicate an excess amount of water at the interface. This was found to signal the onset of debonding. This is an interesting approach but it is not yet predictive in a quantitative sense.

It would be desirable to find a diagnostic test which could be administered to new coatings to evaluate both their short-term qualifications as protective coatings, and also the long-term qualifications under normal cycles of service and storage. We would like a simple test which would correlate well with the magnitude of  $X_B$ . If this very simplistic model is accurate then the swelling of the boundary layer is the principal stress that brings on the delamination. Therefore, a new coating could be evaluated by measuring the force of stress induced by the absorption of water. This could be done by putting the coating on thin metal strips and recording the bending of the strips when immersed in water, saltwater and NaOH solutions of high pH. The greater the curling, the greater the internal stress and, consequently, the greater the delamination rate. It is unlikely, however, that the rate-determining step is simply the swelling of the polymer and we expect that a more realistic solution of the differential equations will reveal a more complicated reliance on other characteristics of the polymer and the substrate.

The long-term qualifications of a new coating can be evaluated by the same test. The kinetics of swelling and deswelling and the kinetics of volume relaxation due to aging have been found to be similar. Knibbe [26] was able to show that most of the stress relaxation in ethylene propylene rubber was ascribable to the rate of diffusion of diluent through the polymer. There is evidence in the literature [27] that one of the consequences of aging under cycling of wet and dry environments is that the free volume in the polymer decreases. The free volume is essentially the space available to a penetrant that will not result in swelling. When the free volume declines, the water that is absorbed has a stronger effect on the swelling action. This indicates that accelerated life testing of the coating could be performed by cycling the polymer through wet-dry environments at elevated temperatures using a simple metal strip curling test as described above.

A blister test technique may be the ultimate way to provide a controlled environment to study the debond process as a function of all the environmental and material variables. A proposal for such a standardized testing instrument has been presented elsewhere [28]. The device could include: a way to circulate a measured amount of electrolyte which has been injected into the interfacial region, forming the blister; a bridge to a standard calomel electrode; a pH probe; a counter electrode (platinum screen); temperature control; and also a compartment for electrolyte or gas over the polymer surface. This kind of testing apparatus could be used for thin and thick films alike. It would be possible to measure current flow due to the cathode reaction as a function all possible parameters. This would give reproducible,



quantitative control over all environmental conditions and different treatments could be compared in a calculated way.

In conclusion, there are two points to be made. First, the testing necessary to establish the model requires only modest experimental work. The second is, once the model has been confirmed, the design of simple tests to evaluate the influence of types of exposures, types of service use, and the response of particular bonding systems, will be relatively easy to arrive at. The close relationship between the model and the test procedure will make possible large improvements in the reliability of projections about the service life of the bonded system.

## CONCLUSIONS AND RECOMMENDATIONS

Degradation of protective coatings is a basic life-limiting problem for sonar equipment. When the goal is to seek a very long extension in the useful life of a unit, reliability studies take too much time and consume too many units. Accelerated life testing is required for long-lived units but the design of such tests requires a sophisticated understanding of the actual mechanisms that contribute to aging and the combination of rate processes altered by the acceleration technique. Projections made about the value of a new application method or a new coating will be uncertain without this kind of detailed understanding of the degradation process.

The key step in improving the reliability of cathodically protected polymeric coatings associated with sonar transducers and the connective cables is fully accounting for the cathodic delamination process. Various mechanisms have been proposed in the literature. Here we have taken the attitude that all of these mechanisms are contributing to one degree or another. The question to be answered is what is the synergistic or combinatorial outcome of these processes. A quantitative model has been proposed based on the kinetics of the chemical processes and the diffusion processes which lead to delamination. The model was solved analytically for rate of delamination under a set of assumptions which simplified the differential equations. However, it would be possible to solve the differential equations without the approximations by numerical techniques.

We strongly recommend that a testing approach for the weak boundary layer model be implemented. This will allow the model to be evaluated and improved to account for all important experimental observations. It will lead to a quantitative relationship between the performance of the coating under test conditions and measureable attributes of the polymer and environment. Finally, it will contribute to the development of improved laboratory testing techniques for the qualification of candidate bonding systems.

In conclusion, we recognize that this kind of detailed mathematical description of the delamination process is an ambitious goal, but it is also something that is greatly needed in the field of polymer bonding technology and, therefore, we believe it would be a profitable course of action.



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